

# A North American and global survey of perfluoroalkyl substances in surface soils: Distribution patterns and mode of occurrence



Keegan Rankin <sup>a,1</sup>, Scott A. Mabury <sup>a</sup>, Thomas M. Jenkins <sup>b</sup>, John W. Washington <sup>c,\*</sup>

<sup>a</sup> Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, M5S 3H6, Canada

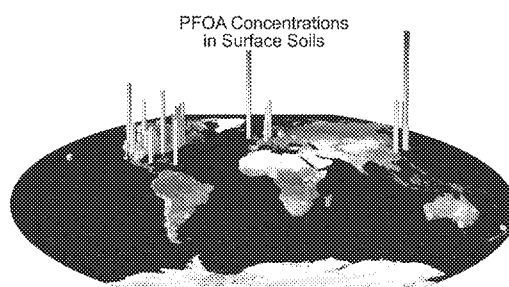
<sup>b</sup> Senior Environmental Employment Program, United States Environmental Protection Agency, 960 College Station Road, Athens, 30605, Georgia

<sup>c</sup> Ecosystems Research Division, National Exposure Research Laboratory, Office of Research and Development, United States Environmental Protection Agency, 960 College Station Road, Athens, 30605, Georgia

## HIGHLIGHTS

- We report on 32 per/polyfluoroalkyl substances (PFASs) in background soils.
- Remote North American sites include Inuvik Canada, La Paz Mexico, Auke Bay Alaska.
- Global includes Antarctica, Mabira Uganda, Vehendi Estonia, Southern Cross Australia.
- Quantifiable concentrations of PFASs were detected in every soil sample.
- Perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) were most common.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The distribution of 32 per/polyfluoroalkyl substances (PFASs) in surface soils was determined at 62 locations representing all continents (North America  $n = 33$ , Europe  $n = 10$ , Asia  $n = 6$ , Africa  $n = 5$ , Australia  $n = 4$ , South America  $n = 3$  and Antarctica  $n = 1$ ) using ultra performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS) systems. Quantifiable levels of perfluoroalkyl carboxylates (PFCA: PFHxA-PFTeDA) were observed in all samples with total concentrations ranging from 29 to 14,300 pg/g (dry weight), while perfluoroalkane sulfonates (PFSA: PFHxS, PFOS and PFDS) were detected in all samples but one, ranging from <LOQ–3270 pg/g, confirming the global distribution of PFASs in terrestrial settings. The geometric mean PFCA and PFSA concentrations were observed to be higher in the northern hemisphere (930 and 170 pg/g) compared to the southern hemisphere (190 and 33 pg/g). Perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) were the most commonly detected analytes at concentrations up to 2670 and 3100 pg/g, respectively. The sum of PFCA homologues of PFOA commonly were roughly twice the concentration of PFOA. The PFCA and PFSA congener profiles were similar amongst most locations, with a few principal-component statistical anomalies suggesting impact from nearby urban and point sources. The ratio of even to odd PFCA was consistent with the atmospheric oxidation of fluorotelomer-based precursors previously observed in laboratory and environmental studies. Given the soils were collected from locations absent of direct human activity, these

\* Corresponding author.

E-mail address: [washington.john@epa.gov](mailto:washington.john@epa.gov) (J.W. Washington).

<sup>1</sup> Present address: Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario, L5K 2L1, Canada.

results suggest that the atmospheric long-range transport (LRT) of neutral PFASs followed by oxidation and deposition are a significant source of PFCAs and PFSA to soils.

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## 1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are surfactant compounds possessing a perfluorinated moiety ( $C_nF_{2n+1}$ ), many of which exhibit high chemical and thermal stability (Kissa, 2001; Buck et al., 2011). Consequently, the very properties that make PFASs ideal for commercial applications also render many persistent and ubiquitous in the environment. Perfluoroalkyl carboxylates (PFCAs) and sulfonates (PFSA) are two groups of PFASs that have received considerable attention due to their widespread detection in precipitation (Taniyasu et al., 2013), water (Yamashita et al., 2005; Ahrens et al., 2009; Benskin et al., 2012), sediment (Higgins et al., 2005; Yeung et al., 2013), wildlife and humans (Giesy and Kannan, 2001; Houde et al., 2006).

Historically, PFCAs and PFSA have been emitted to the environment directly or indirectly through the biotic and abiotic transformation of polyfluorinated precursors (Prevedouros et al., 2006). Distribution of PFCAs and PFSA in the environment also results from a combination of gas- and particle-phase atmospheric long-range transport (LRT) (Ellis et al., 2003; Barber et al., 2007; Schenker et al., 2008). Neutrally charged, volatile precursors, such as fluorotelomer alcohols (FTOHs) and perfluoroalkyl sulfonamides (FASAs), are known residuals in (Dinglasan-Panlilio and Mabury, 2006) and degradation products of surfactants and side-chain fluorinated polymers (Washington et al., 2009; Chu and Letcher, 2014; Rankin et al., 2014; Washington and Jenkins, 2015; Washington et al., 2015), and have been measured globally in the atmosphere (Martin et al., 2002; Stock et al., 2007; Li et al., 2011; Gawor et al., 2014), but evidently are not common at detectable levels in uncontaminated soils (Ellington et al., 2009). Both FTOHs (Ellis et al., 2004) and FASAs (D'Eon et al., 2006) undergo atmospheric oxidation to produce PFCAs and PFSA, respectively (Ellis et al., 2004; D'Eon et al., 2006). Evidence of PFCAs and PFSA in remote and urban precipitation (Loewen et al., 2005; Scott et al., 2006; Filipovic et al., 2015) supports LRT of volatile precursors as a mode of global dissemination. Because PFCAs and PFSA have low acid-dissociation constants ( $pK_a$ ), negligible vapor pressures and relatively high water solubility (Burns et al., 2009; Cheng et al., 2009), it has been posited that oceans are the dominant global PFCA and PFSA reservoir (Prevedouros et al., 2006). Given the collective findings of these and other studies, fluorotelomer manufacturers and the USEPA agreed to phase-out long-chain ( $>C7$ ) fluorotelomer production by January 2015 (EPA, 2010).

While the role of oceans as a long-term reservoir for these legacy compounds has been confirmed, little is known regarding the possible role of soils as long-term sinks for PFASs at the global scale despite knowledge that these compounds sorb to solid matrices (Higgins and Luthy, 2006; Ahrens et al., 2011). Soils are known to be an important sink for other persistent organic pollutants (POPs) such as polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (Harrad et al., 1994; Meijer et al., 2002, 2003; Hassanin et al., 2004; Hassanin et al., 2005). In addition to locally contaminated soils, atmospheric LRT has led to numerous POPs being globally distributed in background soils, making remote background soils a key component in global mass-balance estimates of numerous POPs as well (Meijer et al., 2003). In

contrast, little is known about the content of PFCAs and PFSA in background soils. To date, PFAS studies largely have focused on soils impacted by either the application of contaminated wastewater-treatment biosolids to agricultural fields (Washington et al., 2010; Yoo et al., 2010; Sepulvado et al., 2011) or nearby fluorochemical manufacturing facilities (Davis et al., 2007; Ruan et al., 2010; Wang et al., 2010, 2013), which have PFCA and PFSA concentrations in excess of 100 ng/g. These concentrations are significantly higher than PFCA and PFSA concentrations previously reported ( $<5000$  pg/g) with a few background soils measured in China, South Korea and United States (Washington et al., 2008; Naile et al., 2010; Pan et al., 2011; Wang et al., 2011; Naile et al., 2013). A recent study reported on 60 surface soils from 6 countries (China, Greece, Japan, Mexico, Norway and USA), with an objective of characterizing “background soils,” i.e., avoiding soils having known PFAS contamination (Strynar et al., 2012). The majority of this study's soils were found to have PFAS concentrations falling below the quantitation limit (10.2 ng/g for PFOA and 89.3 ng/g for PFOS), with PFOA not detected in 78% of samples and PFOS not detected 52%.

The present study evaluated the distribution of PFASs in background surface soils, which ideally were distant from obvious human activity, employing variance in replication of samples and blanks to achieve low detection limits with standard statistical methods. Analytes included PFCAs (C6–C14), PFSA (S6, S8, S10), *n*:3 fluorotelomer acids (FTCAs) and unsaturated fluorotelomer acids (FTUCAs; *n* = 5–13 odd), and *m*:2 FTCAs and FTUCAs (*m* = 6–14 even). A collection of 62 samples was obtained from 22 countries, representing all continents, and analyzed for a suite of 32 PFASs. Observed PFCA and PFSA concentrations were then employed to elucidate the distribution of PFASs in terrestrial settings at the global scale and to infer mode of occurrence.

## 2. Materials and methods

### 2.1. Chemicals

A detailed list of all chemicals can be found in the SI, including a tabulation of PFASs analyzed in this study (Table S1).

### 2.2. Soil samples

Soil samples were graciously collected by colleague scientists, who were chosen with the objective of obtaining a wide geographic sample distribution. Sample collectors were requested to sample from a nearby location that they judged to have no evident human impact (or limited impact if “no impact” was not feasible), using a sampling kit we supplied and following instructions supplied with the kit (see SI). Roughly half of the samples were collected from North America, where the study institutions are located (Fig. 1). Each sampling location was assigned an alpha numerical ID based on the continent where they were obtained. A detailed list of all sampling locations can be found in Tables S2–S4 with corresponding maps in Figs. S1–S6. Soil samples were analyzed for total organic carbon (TOC) at University of Georgia laboratories. Discussion is given in the SI, and sample location and attendant data are supplied in Tables S2–S4.

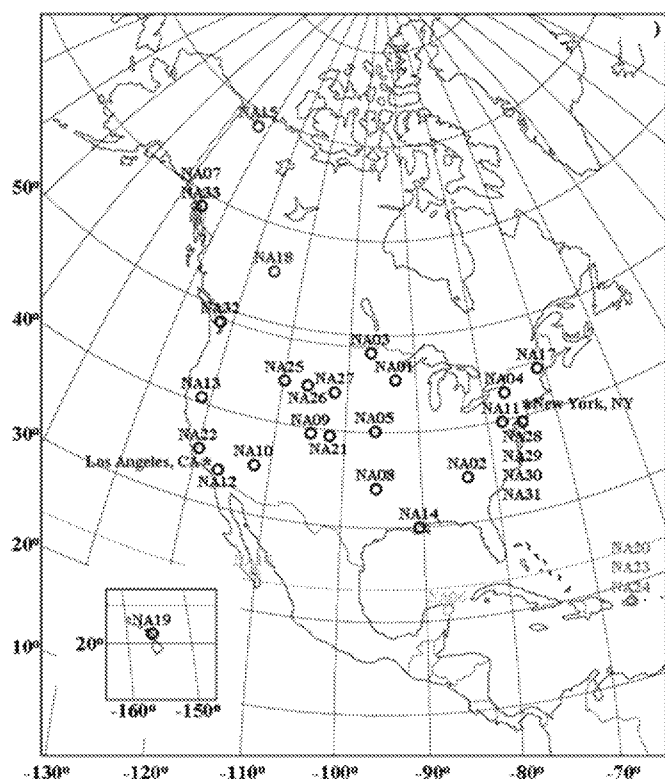


Fig. 1. North American sampling locations.

### 2.3. Extraction method

The extraction method used in this study is based on previous methods (Washington et al., 2007, 2008, 2014), that have been shown to recover roughly 100% of PFOA, perfluorodecanoic acid (PFDA) and perfluorododecanoic acid (PFDoDA) in spike-and-recovery experiments (Washington et al., 2014). Each soil was extracted in triplicate with 5 g (wet weight) samples transferred into methanol-washed polypropylene copolymer (PPCO) centrifuge tubes and sealed with PPCO caps. The soil samples were spiked with 2000 pg  $^{13}\text{C}_8$  mass-labeled perfluorooctanoate (M8PFOA) as a recovery standard (with other mass-labeled standards dedicated to matrix-standard use as described below). A 400  $\mu\text{L}$  aliquot of 2 M sodium hydroxide prepared in polished 18 M $\Omega$  water (PW; SI) and an 8.5 mL aliquot of a 90:10 acetonitrile:PW (ACN:PW) solution were mixed into the soils by vortexing for 15–30 s, sealed with caps and Parafilm, and then sonicated in an ice bath for 60 min. Next, the samples were mounted onto a LabQuake rotisserie mixer and rotated for ~15 h at 8 revolutions per minute then centrifuged at 36.6 kG (17,500 rpm) and 18–22 °C for 15 min. The supernatants were decanted into glass vials and a second round of 90:10 ACN:PW extraction performed on the soils. The two supernatants were combined in the glass vial and blown to near dryness under filtered air in a solid-phase-extraction (SPE) manifold (Fig. S7). The extract matrices were cleaned by dissolution in 4 mL tetrabutyl ammonium hydrogen sulfate (TBAS) ion-pairing solution, extracted into 5 mL of methyl-*tert*-butyl ether (MTBE) by vortexing, and then stored in a freezer overnight (Washington et al., 2014). The TBAS solution was then extracted again with a second 5 mL aliquot of MTBE. The MTBE fractions were decanted into pre-weighed glass vials and blown to dryness in the SPE assembly at room temperature. The glass vials were re-weighed and the dried extracts reconstituted with a 1 mL aliquot of 60:40 ACN:PW containing

100 pg/g of eleven mass-labeled matrix internal standards (6 PFCAs, 3 fluorotelomer acids and 2 PFASs) as described in the SI and previous papers (Washington et al., 2010, 2014). The glass vials were weighed a final time prior to filtering with 0.2  $\mu\text{m}$  Nylon filters.

### 2.4. Instrumental analysis and quantification

Two Waters liquid chromatograph tandem mass spectrometry (LC-MS/MS) systems (Waters Corporation, Milford, MA) were used in the present study. The soil extracts were analyzed for PFCAs and fluorotelomer acids at the USEPA (Athens, GA) using an Acquity UPLC coupled to a Quattro Premier triple-quadrupole mass spectrometer operated in negative electrospray ionization mode. Chromatographic separation was performed using an Acquity BEH C18 column (1.7  $\mu\text{m}$ , 2.1  $\times$  100 mm) at 35 °C with a Waters frit guard disc (0.2  $\mu\text{m}$ , 2.1 mm). Instrumental parameters, methods, calibration and mass-labeled matrix internal standards were detailed in earlier work (Washington et al., 2014), and are summarized in Table S1.

The soil extracts also were analyzed at the University of Toronto (Toronto, ON) for PFASs, and qualitative analyses for % branch chains (by relative peak areas) of PFOA and PFOS. Here, analyses were performed using an Acquity UPLC coupled to a Xevo-TQ-S MS/MS operated in negative electrospray ionization mode. Chromatographic separation was performed using an Acquity BEH C18 column (1.7  $\mu\text{m}$ , 2.1  $\times$  75 mm) at 60 °C. Analytes were quantitated using the mass-labeled internal standards added during reconstitution. Details are described in the SI.

### 2.5. Quality assurance and detection-limit determination

Field blanks (Ottawa sand having known, very-low [PFAS]s) were deployed with each sample collection kit, and exposed to sampling equipment and ambient air at the sample location, to detect contamination arising from sample collection or transit back to the laboratory (see SI). In the lab, each sample was stored in a locked box in a cooler at ~4 °C until extractions began. Samples were prepared by: i) sieving through a methanol-washed, stainless-steel, 2-mm sieve, and mixing with a methanol-washed spatula before withdrawing aliquots for extraction; and ii) extracting three separate aliquots in parallel to characterize the combined effects of soil heterogeneity and analytical uncertainty. Process blanks (i.e., all extraction, cleanup and reconstitution activities carried out in empty centrifuge tubes, then analyzed) were included with each extraction round to characterize analyte concentrations arising from the extraction procedure and associated laboratory activities.

With the objective of achieving low detection limits, the limit of detection (LOD) and limit of quantification (LOQ) were defined using a two-mean Student's *t*-test having common, but unknown variance (Steele and Torrie, 1980):

$$t = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{s_{pooled}^2 \left( \frac{1}{n_1} + \frac{1}{n_2} \right)}} \quad (1)$$

where *t* is the test statistic used to define LOD and LOQ,  $\bar{x}_1$  is the mean of each soil,  $\bar{x}_2$  is the process-blank mean,  $s_{pooled}^2$  is the pooled sample variance, and numbers of observations are given by  $n_1 = 3$  soil replicates and  $n_2 = 10$  process-blanks. The pooled sample variance is defined as (Steele and Torrie, 1980):

$$s_{pooled}^2 = \frac{(n_1 - 1)\Sigma(x_1 - \bar{x}_1)^2 + (n_2 - 1)\Sigma(x_2 - \bar{x}_2)^2}{n_1 + n_2 - 2} \quad (2)$$

To define LOQ and LOD, we compared our calculated values of  $t$  to critical  $t$  values ( $t_{critical}$ ) for a one-tailed  $t$ -test, abbreviated  $t_{\alpha(1),v}$ , where  $\alpha$  is the specified significance level, (1) signifies one-tailed, and  $v$  is the degrees of freedom ( $v = n_1 + n_2 - 2 = 3 + 10 - 2 = 11$ ). The  $t_{critical}$  values we chose were 4.025 at  $\alpha > 0.001$  and 1.796 at  $\alpha > 0.05$ . So we defined LOQ as  $t > t_{0.001(1),11}$  and LOD as  $t > t_{0.05(1),11}$ , meaning there is a respective 99.9% and 95% certainty the observed sample concentration statistically exceeds the process-blank levels. By using this standard statistical approach, we minimize detection limits, albeit at the cost of having unique limits for each sample arising from the sample-specific standard deviation among the three replicates. Sample values exceeding the LOQ are reported herein as blank corrected, i.e., reported soil concentrations are analytical concentrations minus mean process-blank values.

## 2.6. Statistical analysis

Principal component analysis (PCA) was used to evaluate PFAS distributions amongst all sampling locations. The PFAS data were preprocessed by subtracting process-blank means from location means and dividing by location standard deviations as a qualitative correction for heteroscedasticity in the data. The FTCA and FTUCA data were excluded from PCA because many locations had non-detectable levels. PCA was performed using a correlation matrix with Statistica 12 (StatSoft Inc., Tulsa, OK).

## 3. Results and discussion

### 3.1. Quality metrics

Recovery of M8PFOA averaged 108% (78%–132%; SI) indicating satisfactory recovery, consistent with previous studies documenting effective recovery for these methods with C8, C10 and C12 PFCAs (Washington et al., 2014). Most field sand blanks and laboratory process blanks returned low (<20 pg/g) detections supporting the absence of contamination for most sample data (SI). Three field sand blanks (NA23, AF03 and AF05) out of 62 (Table S8), and one laboratory process blank (TB1) out of 11 (Table S9) returned anomalous PFOA concentrations. Examination of all other quality metrics for the samples associated with these blanks suggested no loss of integrity (SI discussion), and most analytical results for these samples did not fall near extremes in the data distribution, so we report these samples here. Nevertheless, results for the eight samples associated with these blanks (AF03, AF05, NA06, NA09, NA11, NA19, NA23, AS01) should be regarded with caution (SI discussion).

### 3.2. PFAS concentrations

Every soil sample in our global survey had quantifiable concentrations of at least three PFCAs, with total PFCAs ( $\Sigma$ PFCAs) ranging from 29 to 14300 pg/g (Table 1; Fig. 2). All samples but one, from rural Estonia (EU09), had quantifiable PFSAs, with  $\Sigma$ PFSAs ranging from <LOQ–3270 pg/g (Table 1; Fig. 2). Detailed descriptions of sample locations and their  $\Sigma$ PFCAs and  $\Sigma$ PFSAs are provided in the SI (Tables S2–S4, Tables S13–S24). Generally, the most abundant congeners were PFOA and PFOS with PFOA concentrations up to 3440 pg/g for a sample from Japan (AS04) and PFOS as high as 3130 pg/g for a sample from Copenhagen, Denmark (EU01). Both PFOA and PFHxA were detected in all samples, and PFOS was detected in all samples except for one Estonian sample (EU09).

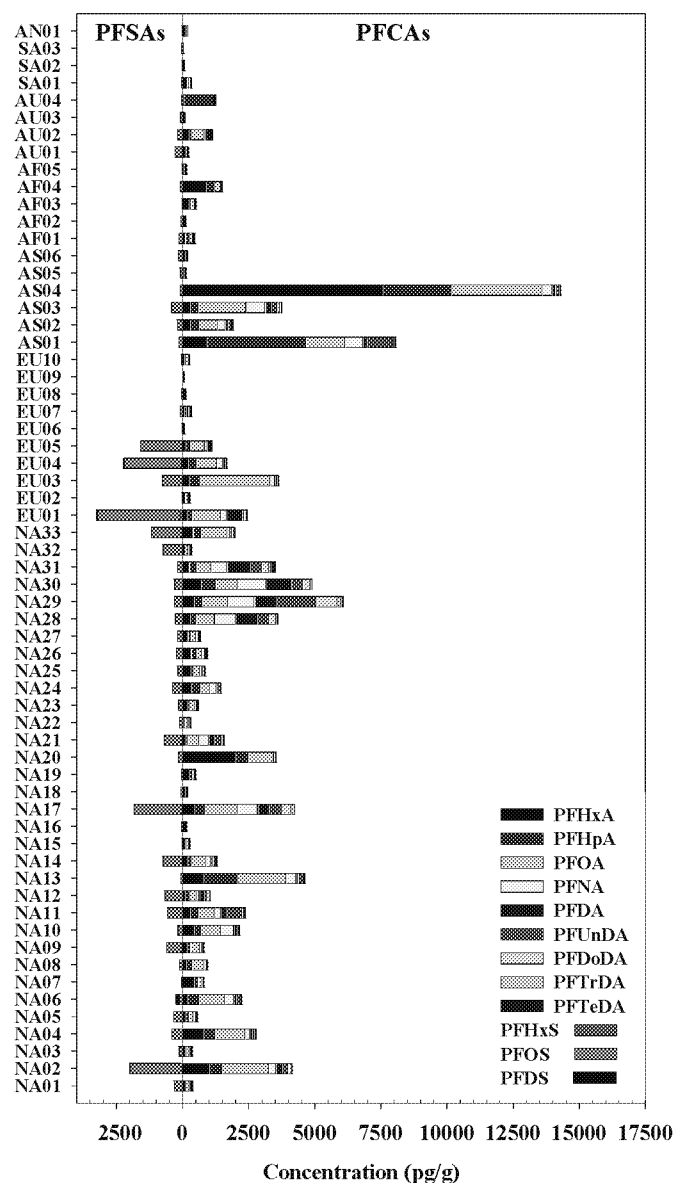
The ubiquity of detections in every one of our 62 samples is noteworthy given the remote isolation of some of our sample

**Table 1**

Continental PFAS concentration ranges in pg/g dry weight with the continental geometric mean in parentheses.

| Continent                                | $\Sigma$ PFCAs      | $\Sigma$ PFSAs     |
|--|---------------------|--------------------|
| North America (NA) (n = 33) <sup>a</sup> | 145–6080<br>(1820)  | 35–1990<br>(410)   |
| Europe (EU) (n = 10)                     | 55–3640<br>(1000)   | <LOD–3270<br>(808) |
| Asia (AS) (n = 6)                        | 129–14300<br>(4710) | 79–421<br>(183)    |
| Africa (AF) (n = 5)                      | 124–1490<br>(548)   | <LOD–144<br>(67)   |
| Australia (AU) (n = 4)                   | 79–1260<br>(673)    | 44–297<br>(154)    |
| South America (SA) (n = 3)               | 29–319<br>(138)     | 26–48<br>(36)      |
| Antarctica (AN) (n = 1)                  | 191                 | 7                  |

<sup>a</sup> Includes a sample from Waimea, Hawaii (NA19).



**Fig. 2.** Overview of global PFCA and PFSA concentrations in North American (NA), European (EU), Asian (AS), African (AF), Australian (AU), South American (SA) and Antarctic (AN) surface soils.

locations. For example, Lake Bonney, Antarctica (AN01) had PFOA = 48 pg/g and PFOS = 7 pg/g, Mapunguwe National Park, South Africa (AF02) had PFOA = 14 pg/g and PFOS = 4 pg/g, Vehendi (Lake Vortsjarv), Estonia (EU09) had PFOA = 15 pg/g and PFOS < LOQ, Inuvik (Northwest Territories), Canada (NA15) had PFOA = 270 pg/g and PFOS = 18 pg/g, and Montevideo, Uruguay (SA02) had PFOA = 44 pg/g and PFOS = 26 pg/g.

With the exception of a few locations having detectable concentrations of fluorotelomer carboxylic acids (FTCAs; 1.6–48.5 pg/g) and unsaturated fluorotelomer carboxylic acids (FTUCAs; 6.1–106 pg/g), most samples were <LOD (Tables S13–S24). Generally, detections of FTCAs and FTUCAs tended to occur in samples having moderate to high levels of PFCAs. FTCAs are products of FTOH atmospheric oxidation (Ellis et al., 2004) and have been detected along with FTUCAs in rain water (Ellis et al., 2004; D'Eon et al., 2006). However, FTCAs and FTUCAs also are known to transform to PFCAs in soil as well, with the majority of spiked compounds often disappearing in about one month or less (Myers and Mabury, 2010), so the absence of detectable levels in most soils studied was not unexpected. Of the background soils having detectable FTCA or FTUCA levels, locations AS01, AS04, NA02, NA13, NA20, NA28–31 and NA33 were most noteworthy having concentrations >20 pg/g. Likely causes of some of these anomalies are explored below.

### 3.3. Global PFCA and PFSA distribution

At the hemispheric scale,  $\Sigma$ PFCAs and  $\Sigma$ PFSA showed sharply contrasting distributions north vs. south of the equator, with a

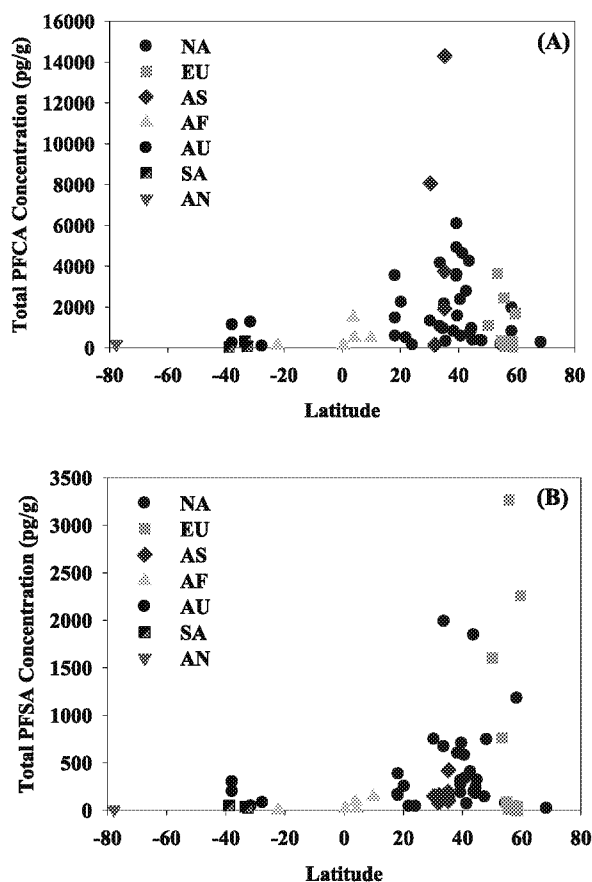


Fig. 3.  $\Sigma$ PFCAs (A) and  $\Sigma$ PFSA (B) plotted against latitude (degrees). Note that higher concentrations of both PFCAs and PFSA >20° in the northern hemisphere.

relatively wide range of values evident in the northern hemisphere, but only comparatively low values in the southern hemisphere (Fig. 3A and B). For the northern hemisphere, the geometric mean values ( $n = 53$ ) for  $\Sigma$ PFCAs and  $\Sigma$ PFSA were 930 and 170 ng/g (ranges of 54.6–14300 and <LOD–3270 pg/g), much in excess of the southern hemisphere which had geometric means ( $n = 9$ ) of 190 and 30 ng/g (ranges of 28.7–1260 and 7.0–300 pg/g), respectively. Similar hemispheric distributions for PFCAs and PFSA have been reported in ocean-water studies ( $n = 60$  & 91 samples) (Ahrens et al., 2009; Benskin et al., 2012), as well as atmospheric studies ( $n = 8$  & 109 samples) for neutral/volatile precursors, such as FTOHs, FASAs and perfluoroalkyl sulfonamide ethanols (FASEs) (Jahnke et al., 2007; Dreyer et al., 2009). While our soil study and these earlier studies on marine water and air are limited in sample number, they all are mutually supportive of a hemispheric imbalance of PFASs, which is consistent with the majority of historical PFCA and PFSA sources being emitted from northern-hemisphere continents (Armitage et al., 2006; Prevedouros et al., 2006; Paul et al., 2009).

Addressing the continental scale, for  $\Sigma$ PFCAs and  $\Sigma$ PFSA summed together, the geometric mean concentrations descended as follows: (Asia, North America) > (Europe, Australia) > (Africa, South America, Antarctica) (Table 1). This pattern is consistent with the hemispheric pattern in that Asia and North America, which have the highest geometric means, are in the northern hemisphere. South America, Antarctica and much of Africa, which occupy the lowest geometric mean grouping, are in the southern hemisphere. Also noteworthy is that, for every continent, the geometric mean  $\Sigma$ PFCA concentrations were considerably larger than the  $\Sigma$ PFSA (Table 1), at least partly because of the larger number of PFCA (9) analytes than PFSA (3).

While some of the higher values in the northern hemisphere might well be affected by local sources, numerous samples having high concentrations were collected from remote and rural locations. For example, the sample from Whipple Dam State Park, PA (NA11), located 250 km northwest of Philadelphia, PA, had  $\Sigma$ PFCA and  $\Sigma$ PFSA concentrations of 2360 and 577 pg/g, respectively; the sample was collected off trail in a long-term forest with no urban or suburban development for kilometers in any direction. The sample from Holderness, NH (NA17), in the rural White Mountains of New Hampshire, had  $\Sigma$ PFCA and  $\Sigma$ PFSA concentrations of 4240 and 1840 pg/g, respectively; this sample was collected off-trail at the very apex of a completely wooded hill. Similarly, the sample from Shasta-Trinity National Forest, CA, located 400 km north of Sacramento, had  $\Sigma$ PFCA and  $\Sigma$ PFSA concentrations of 4618 and 66 pg/g, respectively; this sample was collected in scrubland of a designated national forest.

### 3.4. Principal component analysis (PCA)

The primary sources of variance in our PFCA and PFSA data are depicted in a principal-component score plot (Fig. 4). Of the total variance, the primary component of variation (PC1) contributed 42.59% with PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA and PFTeDA (C9–C14) having the highest loading factors, while the secondary component (PC2) contributed 17.99% with the highest loading factors from PFHxA, PFHpA, PFOA, PFHxS and PFOS (Table S28). So PC1 was dominated by PFCA homologues longer than PFOA, largely degradation products of the telomerization process, and PC2 accounted for variation in PFOA and shorter-chain PFCAs and PFSA.

The majority of samples showed little deviation among one another with 37 of the 62 samples tightly clustered between quadrants 3 and 4 (dashed circle in Fig. 4) and 13 samples falling just outside. The loose clustering of these 37 + 13 = 50 samples indicates similar PFAS profiles for variance optimized by PCA

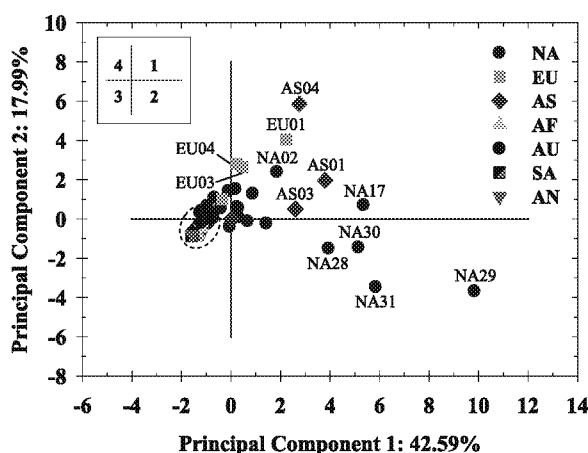


Fig. 4. Principal component score plot of the global PFCA and PFSA surface soil concentrations. The inset shows the numerical ordering of the four quadrants.

analysis, in turn suggesting largely common mode of occurrence and little evidence of pronounced local PFAS sources among these clustered samples.

The remaining 12 samples had more pronounced separation from the cluster with 8 samples (AS01, AS03, AS04, EU01, EU03, EU04, NA02 and NA17) in quadrant 1 and 4 samples in quadrant 2 (NA28–NA31). These 12 PCA outliers fall among the highest  $\Sigma$ PFCA samples in our dataset suggesting that the dominant causes of variation are attributable to samples having elevated PFCA, presumably due to local or regional sources. The outlier samples in quadrant 1 were collected within or near large urban areas and had elevated levels of PFOA and PFOS with the exception of the Asian samples AS01 and AS04, which had elevated PFHxA and PFHpA (Fig. 2). The outlier samples from quadrant 2 (NA28–NA31) were collected from near the municipal water-supply well fields for Penns Grove (NJ), USA, and showed the highest levels of PFNA–PFtEDA (Fig. 2). Presented with this anomalous pattern, we discovered that these Penns Grove samples were collected less than 10 km east of Wilmington, DE, where fluorotelomer-based products were manufactured in the past.

### 3.5. Inferred mode of PFAS occurrence

Given the remote location of many of our sample sources (e.g., Antarctica; Mapungu National Park, South Africa; Vehendi, Estonia; Inuvik, Canada), and clustering of most samples in PCA analysis suggesting a common mode of occurrence, the ubiquitous detection of PFCA and PFSA confirms that LRT plays an important role in the fate of PFASs. This ubiquitous detection in remote soils also is consistent with the observation that PFCA homologues of C8 and longer tend to remain bound in surface soils (Washington et al., 2010), rather than leaching to depth, so that observed concentrations can be expected to be a function of the source term more so than loss from leaching. While there is consensus that PFASs are subject to LRT, some uncertainty remains regarding the principal mode of LRT, with some emphasizing atmospheric transport and deposition (Ellis et al., 2003; Barber et al., 2007; Schenker et al., 2008), and others focusing on direct release of PFASs (Prevedouros et al., 2006).

Addressing expectations for atmospheric transport, transformation of the volatile n:2 FTOH precursors of PFCA by Cl atoms (as surrogates for OH radicals) was studied in smog chambers, and the dominant reaction products were found to be roughly

equimolar (n–1) and n PFCA along with lower yields of shorter-chain homologues (Ellis et al., 2004; Wallington et al., 2006). For example, 8:2 FTOH formed roughly equimolar PFOA (n–1) and PFNA (n), along with lesser quantities of PFHpA and PFHxA (Ellis et al., 2004). However, in the presence of elevated  $\text{NO}_x$  levels (typical of urban settings) a gas-phase unzipping mechanism generates (n–1) PFCA preferentially over n PFCA (Ellis et al., 2004; Wallington et al., 2006). Likewise, investigating heterogeneous atmospheric photooxidation of n:2 FTOHs on typical atmospheric particulates, Styler et al. (2013) also reported enriched (n–1)/n PFCA yields, up to ~6/1. Taken together, these investigations document that the ratio of (n–1)/n PFCA arising from atmospheric oxidation of n:2 FTOHs commonly can be expected to range from 1/1 to as high as ~6/1.

Regarding direct PFCA emission, Prevedouros et al. (2006) reported that direct global emissions in the year 2000 yielded a PFOA/PFNA ratio of 8/1. Biological degradation of n:2 FTOHs to PFCA has been shown to proceed through beta oxidation to yield (n–1) PFCA greatly in excess of n PFCA; for example, 8:2 FTOH degrades to form the (n–1) PFCA of PFOA (Wang et al., 2009). Taking these observations together, direct release of PFCA and biological degradation of FTOHs in terrestrial or aquatic ecosystems should produce (n–1)/n PFCA ratios of  $\geq 8/1$ . Conversely, absent some additional complicating factor, (n–1)/n PFCA ratios  $< 8/1$  are inconsistent with oceanic transport as the dominant mode of LRT. Addressing direct release of shorter-chain homologues, Prevedouros reported the 2000 emissions to be quite low relative to PFOA, PFHxA/PFOA ~0.005 (Prevedouros et al., 2006), and the direct emissions of long-chain PFCA, including PFDA and longer, to be quite low relative to PFOA as well (Prevedouros et al., 2006).

Examining our data in light of these diagnostic homologue patterns, in a plot of the PFOA/PFNA ratio as a function of  $\Sigma$ PFCA (Fig. 5), a substantial majority of the samples fall in the PFOA/PFNA = (1/1 to 6/1) range expected for atmospheric transport and oxidation of FTOHs, consistent with the PCA loading of PFOA and PFOS on PC2 instead of PC1 with longer-chain PFCA. Among the samples defining the low end of this range are the four samples from Penns Grove, NJ (NA28–NA31), which were unique in the PCA plot, lying far from the origin in quadrant 2 (Fig. 4). Given the close proximity of samples NA28–NA31 to a major fluorotelomer manufacturing facility, the near equimolar (n–1)/n PFCA observed

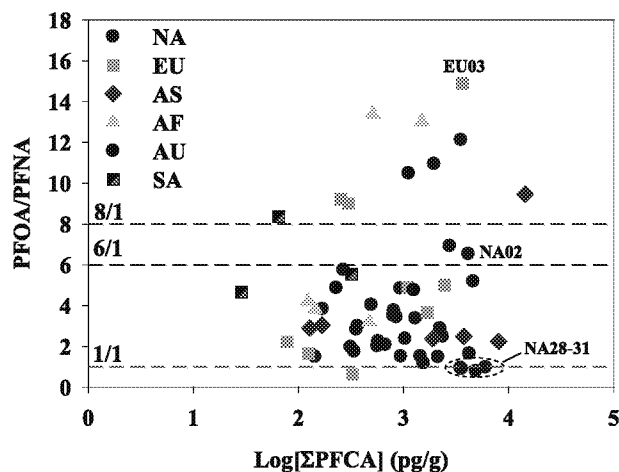


Fig. 5. Ratio of PFOA to PFNA versus log scale of  $\Sigma$ PFCA concentrations for all sampling locations. Dashed 1/1 and 6/1 lines are assumed to represent gas phase oxidation of PFAS precursors, and the lower stoichiometric bound for direct emission of PFCA (Direct 8/1). Note that locations AN01, AU03 and EU09 were excluded because PFNA was either  $< \text{LOQ}$  or  $< \text{LOD}$ .

in these samples (Table S13) likely result from the gas-phase oxidation of fluorotelomer-based precursors by OH radicals (Ellis et al., 2004; Wallington et al., 2006). It is noteworthy that the PFOA/PFNA = (1/1 to 6/1) range of the majority of our samples also is consistent with the homologue distributions previously observed in rainwater from rural and remote locations (Scott et al., 2006), Arctic glacial ice (Young et al., 2007) and lakes (Stock et al., 2007). Given the remoteness of samples for these previous studies and many of the soils in the present study, and dominant range of PFOA/PFNA = (1/1 to 6/1), LRT of neutral fluorotelomer precursors followed by gas-phase oxidation, and wet or dry deposition seems to be the dominant source of the PFCAs in these samples.

Several soils from the present study had PFOA/PFNA ratios >8/1 (Fig. 5). While some of these soils were collected close to urban areas, and possibly reflect FTOH oxidation in the presence of high [NO<sub>x</sub>] or direct emission of PFCAs from nearby sources, the PFOA/PFNA ratio of these samples also is in the range that is consistent with ocean transport of PFCAs and PFASs (Armitage et al., 2006; Prevedouros et al., 2006). In an effort to elucidate a possible role of ocean transport, we plotted the PFOA/PFNA ratio for the Antarctic sample (AN01), and the 12 samples having  $\Sigma$ PFCAs lower than AN01 against distance from ocean water. Four samples located within 100 km of marine waters had PFOA/PFNA ratio >8/1, but none of the samples >100 km from marine waters had the >8/1 ratio, suggesting any role for marine-aerosol mode of LRT of PFASs in terrestrial soils tends to be restricted to near-coastal regions (Fig. S14).

Looking at the PFHxA/PFOA ratio of the 13 lowest PFCA samples depicted in Fig. S14, mean PFHxA/PFOA = 1.44 (range = 0.22 to 6.0), close to 300x that of the production ratio reported by Prevedouros et al. (Prevedouros et al., 2006); this high ratio suggests a mode of PFHxA occurrence other than direct production and release, e.g. degradation of PFHxA precursors (Liu et al., 2010).

Addressing the long-chain PFCAs, 58 of 62 samples in our survey had detectable levels of one or more PFDA–PFTrDA (Tables S13, S17 and S21), with approximate PFDA/PFUnDA and PFDoDA/PFTrDA ratios of 2 and 4, respectively. Based on the low historical direct-production rate of these compounds, this observation also supports oxidation of precursors as the major mode of occurrence for these PFCAs, and these results are consistent with previous detections of PFDA–PFTrDA in rainwater (Scott et al., 2006), Arctic glacial ice (Young et al., 2007) and lakes (Stock et al., 2007) in remote locations.

Recent studies have confirmed that fluorotelomer-based polymers (FTPs) degrade with decades-scale half-lives (Rankin et al., 2014; Washington and Jenkins, 2015; Wallington et al., 2015), and could be a significant indirect source of FTOHs to the environment, especially C10 (i.e., 10:2 FTOH) and longer compounds which dominantly were produced for use in fluorotelomer products (Wang et al., 2014). Considering this newly confirmed source of FTOH precursors to PFCAs together with the above observations, atmospheric migration and oxidation of FTOHs evidently is a dominant mode of LRT to remote inland environments.

### 3.6. Environmental implications

Given that our sample set included representatives from some of the most undeveloped and farthest reaches of terrestrial Earth, and every surface soil that we tested had quantifiable concentrations of at least two PFASs, this study demonstrated that PFASs are ubiquitous in background soils.

Because roughly 30% of Earth's surface is terrestrial, the data we present here confirm that soils are a major repository for PFASs at the global scale. The ratios of (n–1)/n PFCAs observed are generally consistent with the gas-phase oxidation of volatile precursors as

the dominant mode of LRT, albeit, perhaps with some influence from ocean transport in coastal regions. This finding of a dominant atmospheric mode of occurrence may have important implications for potential future PFAS releases to the environment because landfills commonly combust/vent generated gases to the atmosphere (Weinberg et al., 2011). To the extent that volatile fluorotelomer compounds generated from landfilled waste are vented like other landfill gases, disposed consumer goods could constitute a large source term of PFASs to the environment in the decades to come (Washington and Jenkins, 2015). Finally, considering that PFASs can enter plant (Yoo et al., 2011) and animal (Lasier et al., 2011) tissue from soils and sediments, these data document that toxic and persistent PFASs are potential components of terrestrial ecosystems at the global scale.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2016.06.109>.

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